

Observation of the Inverse Piezoelectric Effect in Polyethylene while under a Polarising Field

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The inverse piezoelectric effect has previously been reported in polymers such as PVC and PMMA [1] and even such amorphous materials as wood and bone [2]. The following work has confirmed that PVC will show the effect, as will polyethylene. A direction of anisotropy was introduced into the samples by a polarising voltage, and results for the value of the piezoelectric g constant against the polarising field are given for a sample of polyethylene.

1. Introduction

Previous work has shown that the piezoelectric effect is to be expected in some polymers [3, 4].

The direct piezoelectric effect appears to be a suitable charge producing mechanism which could explain the causes of the microphony which is still observable in anti-microphonic cables. It is known that low density polyethylene consists of 50 to 60% crystalline regions, and that these regions are orientated in the direction of draw when a cable is manufactured. However, for ease of measurement, this initial work has used an applied polarising field to introduce a direction of anisotropy into the polyethylene. On applying an alternating excitation voltage to the sample while it was polarised, it was expected that the sample would mechanically vibrate at the applied resonant frequency.

By showing that the effect observed was linear and dependent on the direction of the applied field, it was evident that it was the piezoelectric, and not the electrostrictive, effect that was being observed.

A piezoelectric constant of the order of 100×10^{-3} V metre/Newton was found for an applied field of about 150 kV/cm. This compares with 24.8×10^{-3} V metre/Newton for PZT 5A, and the order of 180×10^{-3} V metre/Newton for Rochelle Salt. However, it cannot be inferred from this that the material could be a better

piezoelectric element (i.e. efficient charge to strain converter) than the above materials. For the same geometry PZT 5A has a capacitance 5×10^2 higher than polyethylene, so that for the same driving voltage much less charge can be placed on the polyethylene. The relevance of this is apparent from the definition of the piezoelectric g constant in section 3.

2. Experimental Method

A holder was designed so that the polyethylene disc sample could be excited by an alternating voltage while under a large DC polarising field. There were two holders mounted such that the faces of the polyethylene transmitting disc and the PZT ceramic receiver were placed plane parallel to each other, with a separation of about 4.5×10^{-2} m. The intervening medium was an insulating fluid, transformer oil, so that the stress wave transmitted could be picked up by the receiver and the possibility of spark breakdown in the transmitter was reduced. See fig. 1.

It can be shown that for a circular source of radius a , having a plane radiating surface oscillating as a piston with SHM, the variation of intensity, I , with distance, d , along the axis is given by

$$I = I_0 \sin^2 \left[\frac{\pi}{\lambda} (\sqrt{d^2 - a^2} - d) \right]$$

when $d \gg a$ then

$$\sin^2 \left[\frac{\pi}{\lambda} (\sqrt{d^2 - a^2} - d) \right] \rightarrow \frac{\pi a^2}{2\lambda d}$$

The Fraunhofer zone which diverges at semi-angle $\theta = \tan^{-1} \lambda/a$ occurs when $d > a^2/\lambda$. Hence for a near parallel beam $a \gg \lambda$ (see fig. 2).

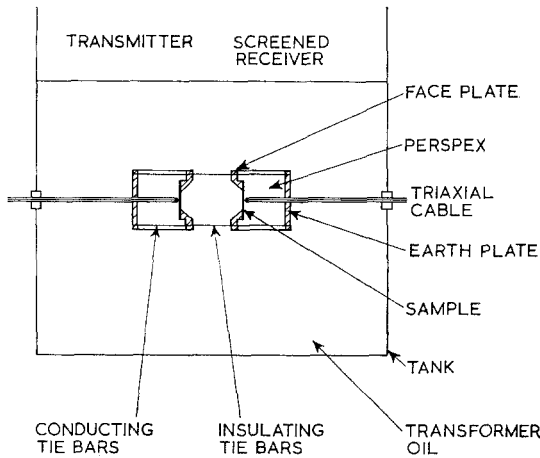


Figure 1 Experimental apparatus.

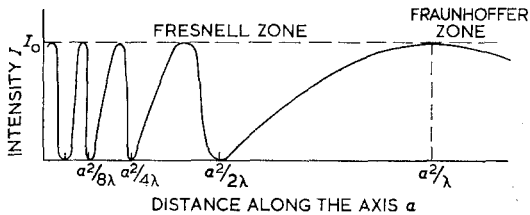


Figure 2 Intensity I of acoustic wave with distance along the axis d .

The DC voltage was applied to the sample on the centre conductor of a triaxial cable, the alternating voltage being applied to the inner braid, so that it was capacitive coupled onto the centre conductor and so appeared on the polymer sample.

The sample had an electrode of indium approximately 5000 \AA thick evaporated onto each face, one face being earthed and the other having the voltage applied to it.

3. Resonant Frequency and Piezo Constants

The frequency at which we would expect the polymer sample to resonate is simply known from the thickness t , and other fundamental

constants of the material. According to the formula for a half wave oscillator the frequency

$$\nu = \frac{C}{2t} \quad (1)$$

where C is the velocity of propagation and

$$C = \left(\frac{1}{S\rho} \right)^{\frac{1}{2}} \quad (2)$$

where S is the compliance and ρ the density of the material.

If we define the axis of polarisation as the 3 direction (the 1 and 2 axes follow in a right-handed set of co-ordinates), then the electrodes are perpendicular to this and S_{33}^D becomes the quantity of interest. The first subscript denotes the direction of the stress, the second that of the strain, and the superscript that it is measured with the electrodes open-circuited. Hence,

$$\nu = \frac{1}{2t(S_{33}^D\rho)^{\frac{1}{2}}} \quad (3)$$

Putting in a value of $5.0 \times 10^{-4} \text{ m}$ for the sample thickness used, and 1300 m/sec as the value of the velocity of sound in PVC, then equation 1 will yield a value for the resonant frequency of 1.3 MHz which we will be able to check.

The piezoelectric d constant is defined as the

$$\frac{\text{charge developed/unit area}}{\text{stress applied}} = \frac{Q/A}{\sigma}$$

and the g constant as

$$\frac{\text{strain developed}}{\text{charge supplied/unit area}} = \frac{e}{Q/A}$$

Again these constants are referred to axes so that the constant we are able to determine is g_{33} . The constant d_{33} is known for the ceramic receiver as is the output voltage, so we are able to determine the charge developed. Hence the stress applied is found. From a calibration of the system using two known ceramics (as transmitter and receiver), the loss in the tank can be determined so that the stress produced by the polymer is known. This is related to the strain developed by the compliance. Hence the unknown g_{33} constant can be determined. The actual quantities measured were the output voltage from the ceramic and the input voltage to the polymer sample. The measured output voltage from the system was $V_2 \text{ V}$. The total amplifier gain was G and the attenuation due to capacitive coupling of the signal was A_2 .

Hence the signal from the ceramic

$$= \frac{A_2 V_2}{G} V.$$

The charge/unit area from the ceramic

$$= \frac{A_2 V_2 C_2}{a_2 G}$$

where a_2 is the area and C_2 the capacity of the ceramic. The stress applied to the ceramic

$$\sigma_3^c = \frac{A_2 V_2 C_2}{a_2 G d_{33}}$$

The attenuation of the stress wave in the system $= \alpha$. Hence the stress at the polymer

$$\sigma_3^P = \frac{\sigma_3^c}{\alpha} = \frac{A_2 V_2 C_2}{a_2 G d_{33} \alpha}.$$

Strain at the polymer

$$e_3^P = \frac{S_{33} D A_2 V_2 C_2}{a_2 G d_{33} \alpha}.$$

Substituting for the compliance

$$= \frac{A_2 V_2 C_2}{4t^2 \rho v^2 a_2 G d_{33} \alpha}.$$

However,

$$g_{33}^P = \frac{e_3^P a_1}{A_1 V_1 C_1}$$

where V_1 is the input voltage, C_1 the polymer capacity, a_1 the area and A_1 the attenuation due to capacitive coupling on the input. Hence

$$g_{33}^P = \frac{A_2 C_2 a_1}{A_1 C_1 a_2 4t^2 \rho v^2 G d_{33} \alpha} \times \frac{V_2}{V_1}. \quad (4)$$

4. Results

The oscilloscope trace shown in fig. 3 is the voltage output from a piece of birmorph ceramic of resonant frequency 660 kHz when a 100 V amplitude step has been applied to a PVC sample while under a -20 kV polarising voltage.

The waveform can be seen to be made up of two components: an initial high frequency one of 1.4 MHz which agrees with the previous calculated resonant frequency of the sample, and the second dominant frequency of 660 kHz of the ceramic.

As a check that a stress wave was being transmitted, an absorbent material, expanded polystyrene, was placed between the transmitter and the receiver and the signal thereby cut off. A time delay of about 9 μ sec is also shown. This was the

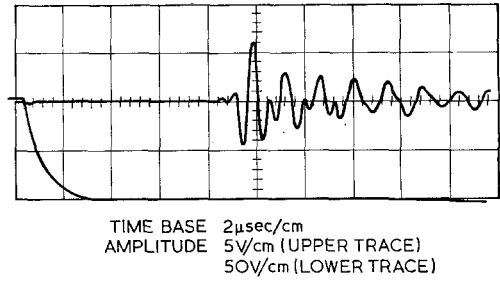


Figure 3 Output from Bimorph ceramic showing transport delay when PVC excited by 100 V step input.

time taken for the stress wave to travel from the transmitter to the receiver.

It was found that the output was very dependent upon the axial position of the bimorph which indicated that the receiver was in the Fresnel zone. After this initial test, which confirmed that PVC showed piezoelectric behaviour, the system was changed to a polyethylene transmitter and a ceramic disc receiver.

The graph in fig. 4 shows the output voltage obtained from a ceramic disc against the EHT applied to the polyethylene sample; the input voltage to the sample being a sine wave remaining constant at 10 V RMS. The fact that the actual points did not go through zero was due to "noise" in the receiving equipment. The resonant frequency of the disc ceramic was 1.25 MHz and the frequency of the sine wave oscillator on the input was adjusted to give a maximum output from the ceramic.

It was noted that when the direction of the applied polarising field was changed there was a 180° phase change in the output signal from the ceramic. This showed that the effect was dependent on the direction of the applied field.

Fig. 5 shows the output voltage obtained from the ceramic against the input voltage to the polyethylene disc for a fixed polarising voltage of -20 kV on the sample.

By substituting the values given in table I into expression 4 we can obtain the relation

$$g_{33}^P = 3.89 \pm 0.79 \frac{V_2}{V_1} \text{ V metre/Newton}$$

By applying this to fig. 4 we can obtain a graph of the electric field against the piezoelectric "constant" of polyethylene for a constant input excitation signal, as shown in fig. 6. The constant is conventionally so called, but it is in fact dependent upon the degree of anisotropy present in the

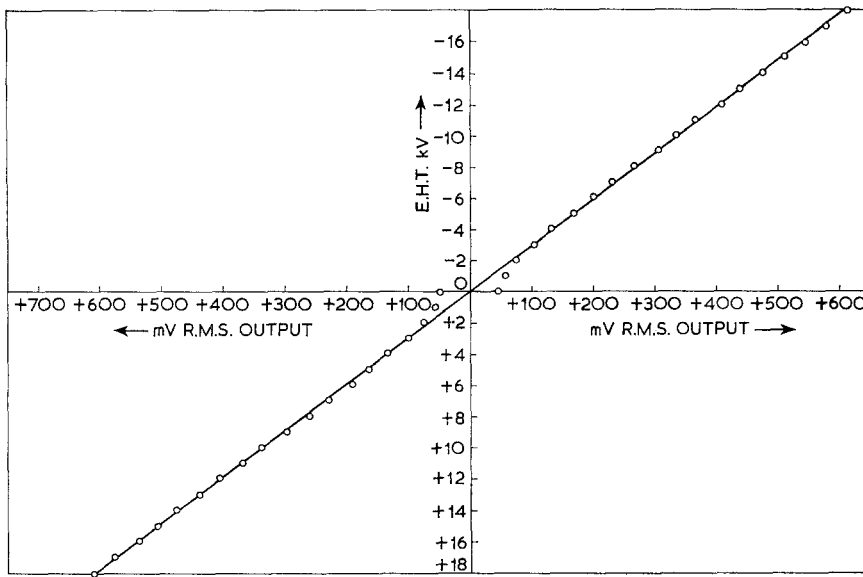


Figure 4 EHT to polyethylene against ceramic output for a constant excitation voltage to the transmitter.

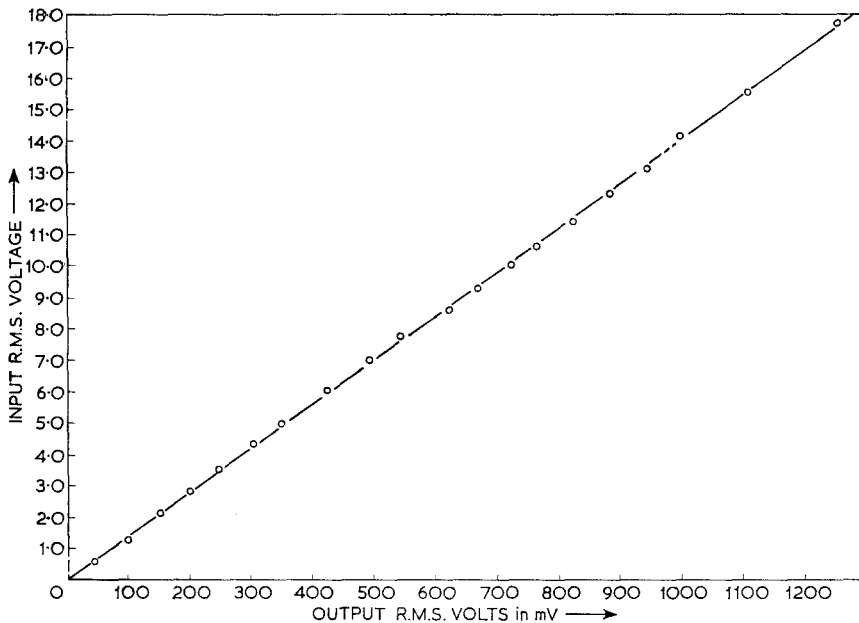


Figure 5 Input voltage to polyethylene against output form ceramic for a constant polarising voltage of - 20 kV.

material, which in this case can be altered by varying the polarising field.

5. Inverse Piezoelectricity and Electrostriction

Very generally, any interaction between an electric field and a dielectric which is in that field and deformed due to the presence of the field is

electrostriction. In this sense the inverse piezoelectric effect is a manifestation of electrostriction. Usually, though, the term electrostriction is reserved for the effect where the deformation is independent of the direction of the field and, most important, proportional to the square of the field. The electrostrictive effect is extremely small.

TABLE I

G = amplifier gain at the receiver	$= (2.23 \pm 0.03) \times 10^4$
A_2 = attenuation at the receiver	$= 6.66 \pm 0.06$
C_2 = capacity of the ceramic	$= (4500 \pm 50) \times 10^{-12} \text{F}$
a_2 = area of the ceramic	$= (4.91 \pm 0.07) \times 10^{-4} \text{m}^2$
d_{33} = piezoelectric constant of ceramic	$= 374 \times 10^{-12} \text{mV}^{-1}$
a = attenuation in the tank	$= 0.1 \pm 0.01$
t = thickness of polymer sample	$= (5.46 \pm 0.06) \times 10^{-4} \text{m}$
ρ = density of polymer	$= 908 \pm 4 \text{kG m}^{-3}$
ν = resonant frequency	$= (1.401 \pm 0.002) \times 10^6 \text{sec}^{-1}$
A_1 = attenuation at the transmitter	$= 0.794 \pm 0.025$
C_1 = capacity of the polymer	$= (8.3 \pm 0.1) \times 10^{-12} \text{F}$
a_1 = area of polymer	$= (5.31 \pm 0.07) \times 10^{-4} \text{m}^2$

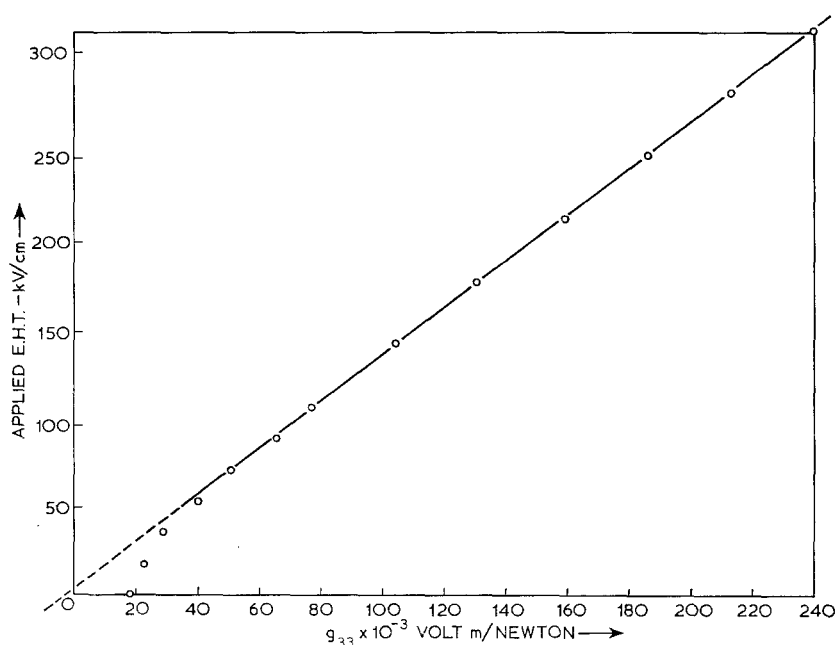


Figure 6 Piezoelectric constant of polyethylene against applied polarising field for an applied signal of 10 V rms.

If the relation between the field and the deformation is linear, then the effect is piezoelectric.

Fig. 5 shows beyond doubt that the effect being observed is a linear one and therefore piezoelectric.

6. Conclusions

It has been shown that polyethylene (and also PVC) show piezoelectric behaviour when a direction of anisotropy is present, in this case caused by an imposed polarising field. The dipole polarisation may arise from C=C bond moments and impurity moments. The CH bond moments are small and, due to the molecular arrangement,

they cancel out. The C=C moments have a value of 0.3 Debye units [5], but they only occur in small concentrations, so the majority of the contribution may be expected to arise from impurity moments. A corollary of this work is the possibility of forming polyethylene elastomers, i.e. freezing in a direction of anisotropy by cooling a sample down while in a strong electric field, or by imposing a direction of anisotropy by mechanical drawing of a specimen and seeing whether this will manifest the piezoelectric effect. The results obtained from a mechanically orientated specimen will be presented in a subsequent paper.

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Letters

Mechanical Behaviour of Polycrystalline TaC

The behaviour of tantalum carbide subjected to compressive loading has been investigated at temperatures above 1200°C *in vacuo*. Previously, Kelly and Rowcliffe [1] had reported a ductile-brittle transition at ~ 1750°C for polycrystalline TaC. In their study employing four point bend tests, they noted further that even at 2000°C only small permanent strains (~ 0.1%) could be achieved prior to failure. An increase in the ductile-brittle point with increase in carbon content was reported by Johansen and Cleary [2] with a temperature range of 1750° to 1925° for C:Ta ratios of 0.90 to 0.981. The present study indicates that significant plastic deformation is achieved at temperatures of 1280°C and above employing three decades of strain rates from 5×10^{-3} to 5×10^{-4} min⁻¹.

The material tested had a C:Ta ratio of 0.95 : 1, an average grain size of 13 μm, and was ~ 93% of theoretical density. The stock from which test samples were obtained was fabricated by vacuum hot pressing [3] in the absence of binder materials. Characterisation of the starting powder (identified as batch 1) and the hot pressed material has been reported previously [3]. In that study, grain boundary segregation of oxygen impurities was noted to occur after 2400°C vacuum heat treatment. Room temperature tensile strength and Young's modulus have also been determined in identical materials and found to be 35000 psi and 39×10^6 psi respectively [4].

At temperatures below 1280°C at the highest strain rate (5×10^{-2} min⁻¹), this material ex-

hibited brittle failure; however, at 1280°C and above, plastic deformation occurred, with permanent strains > 5% being achieved. The yield points of this material exhibited increasingly ductile characteristics at the higher temperatures ($T \geq 1640^\circ\text{C}$), while the onset of plastic flow was indicated by small deviations below 1640°C. The yield stresses were depressed over the entire temperature range, and deformations up to 40% were achieved above 1640°C. The mechanical data were analysed in terms of the relationship:

$$\sigma_{\text{yld}}^n = A \dot{\epsilon} \exp(Q/RT).$$

where $\dot{\epsilon}$ is the strain rate, Q is the apparent activation energy, T is the absolute temperature, n is the stress exponent, A is an empirical constant, R is the gas constant and σ_{yld} is the yield stress. Plotting in terms of $\ln \sigma_{\text{yld}}$ versus $1/T$ at constant strain rates yields parallel, linear fits of these data (fig. 1). Slope changes occur at 1455°C ($0.43T_m$) at the lowest strain rate and at 1640°C ($0.47T_m$) for a strain rate of 5×10^{-3} min⁻¹. The apparent activation energies were determined to be 96 Kcal/mole and 90 Kcal/mole for the high and low temperatures ranges, respectively, based on stress exponents, n , of 4.5 and 13.3 computed for these same regions from $\ln \dot{\epsilon} - \ln \sigma_{\text{yld}}$ relationships at constant temperatures. The activation energy values are consistent with those reported for self diffusion of carbon in TaC (85 Kcal/mole [5] or 98 Kcal/mole [6]). Steinitz suggests that diffusion of tantalum controlled creep rates in his observations on TaC and reported an activation energy of ~ 170 Kcal/mole [7].